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(54) CATALYST CARRIER HAVING CORDIERITE-BASED CERAMIC HONEYCOMB STRUCTURE AND METHOD OF PRODUCING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a lightweight honeycomb structure which is light in comparison with other honeycomb structures even when the thickness is the same by increasing porosity in the cell wall and to obtain a catalyst carrier having a ceramic honeycomb structure, which can be rapidly heated and has sufficient mechanical strengths.

SOLUTION: The catalyst carrier having the cordierite-based ceramic honeycomb structure is characterized by that the volume of pores having diameters of 0.5 to 2 μm is $\geq$30% of the total pore volume, the volume of pores having diameters of 5 to 10 μm is $\leq$20% of the total pore volume, the volume of pores having diameters of $\leq$10 μm is $\leq$30% of the total pore volume, the porosity is $\geq$35%, the A-axis compressive strength is $\geq$18 MPa and the mass per carrier volume containing cell spaces is $\leq$400 g/l.

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CLAIMS

[Claim(s)]
[Claim 1] With the honeycomb structure object with which the principal component of a crystal phase consists of a nature ceramic of cordierite The total pore volume of pore with a diameter of 0.5-2 micrometers 30% or more of total pore volume The total pore volume of pore with a diameter of 5-10 micrometers is [the total pore volume of pore with a total pore volume / 20% or less of / and a diameter of 10 micrometers or more] 30% or less of total pore volume. Support for nature of cordierite ceramic honeycomb structure catalysts characterized by the mass per [in which A axial compression reinforcement includes / porosity / 18 or more MPas and cell space 35% or more] support volume being 400g/l. or less.
[Claim 2] The manufacture approach of the support for nature of cordierite ceramic honeycomb structure catalysts which carries out mixed kneading of the cordierite-ized raw material, and is characterized by making a programming rate later than the programming rate [within the area] till then more than 50 degrees C / Hr in the manufacture approach of the support for nature of cordierite ceramic honeycomb structure catalysts calcinated after extrusion molding on a honeycomb structure object in the middle of the temperature up in the temperature field to which the solid phase reaction of said honeycomb structure object goes.
[Claim 3] The manufacture approach of the support for nature of cordierite ceramic honeycomb structure catalysts according to claim 2 characterized by making the programming rate for 1250-1300 degrees C later than the programming rate for 1200-1250 degrees C more than 50 degrees C / Hr in about 1200-1300 degrees C which is the temperature field to which the solid phase reaction of a honeycomb structure object goes.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the support for nature of cordierite ceramic honeycomb structure catalysts used for an exhaust gas purge, and its manufacture approach.
[0002]
[Description of the Prior Art] Implementation of the emission-gas-purification engine performance which excelled in the exhaust gas purge using the support 1 for ceramic honeycomb structure catalysts of the quality of cordierite as shown in drawing 3 more than before is expected with the request of the discharge total amount reduction by the latest exhaust gas toughening of regulations. The presentation of the support 1 for ceramic honeycomb structure catalysts which uses quality of cordierite as a principal component mainly consists of SiO_2, aluminum$2O_3$, and MgO. In the exhaust gas purge using such support 1 for ceramic honeycomb structure catalysts, at the time of the cold start which is in the condition which started the engine from between the colds, since the catalyst has not got warm yet, it is not activated, but its purification effectiveness of exhaust gas is remarkably low. For this reason, it considers as the problem of the utmost importance for early activation of the catalyst at the time of a cold start to clear emission control. In order to solve such a technical problem, recently, by making it small, the mass, i.e., the bulk density, including making thin thickness of the cell wall 3 for forming the cell space 2 of the support 1 for ceramic honeycomb structure catalysts, or cell space per support volume, the heat capacity of this support 1 for ceramic honeycomb structure catalysts is reduced, and the technique which raises the quick warming of a catalyst is adopted.
[0003] Moreover, the fall of the bulk density by raise in porosity is also effective in raising the quick warming of a catalytic converter, and also in order to support catalyst matter, such as an activated alumina and platinum, so much further, it is one of the important properties to make support 1 for ceramic honeycomb structure catalysts into porosity, i.e., high porosity.
[0004] For the purpose of offer of the support for honeycomb structure catalysts of the low-fever expansion which has the low porosity level which can moreover be satisfied with a thin wall of a strength property, porosity is 30% or less and the support for cordierite honeycomb structure catalysts more than 200kg/cm2 (19.6MPa) is indicated for the compressive strength (A axial compression reinforcement) of the direction of passage of a honeycomb structure object by JP,4-70053,B. To trial No.6, among the example of this official report, in the case of the cellular structure of 102 micrometers of cell wall thickness, and cel consistency 93 cel / cm2 Although the mass per [in which 25.4% of porosity and A axial compression reinforcement are indicated to be 263kg/cm2 (25.8MPa), and include cell space] support volume is unstated, by count from a cel consistency, and cell wall thickness and cordierite true specific gravity 2.52 The support for cordierite honeycomb structure catalysts which the mass per [including cell space] support volume becomes in 1. and 350g /is indicated. And in real use of the support for honeycomb structure catalysts, A axial compression reinforcement which can be borne also on a severe service condition is indicated to have become possible to design the cellular structure of the catalyst support which shows the level of 19.6 or more MPas.
[0005] Moreover, it aims at offer of the suitable cordierite structure to use it for JP,6-69534,B as honeycomb structure catalyst support with little thermal-shock-resistance degradation by support of

an activated alumina with a larger coefficient of thermal expansion than cordierite support, and other catalyst components. The porosity of a honeycomb structure object exceeds 30%, it is 42% or less and the cordierite honeycomb structure object whose pore volume with a diameter of 10 micrometers or more the total pore volume of pore with a diameter of 0.5-5 micrometers is 10% or less of total pore volume in 70% or more of total pore volume is indicated. To trial No.3, it sets among the example of this official report at cylindrical shape cordierite honeycomb structure catalyst support with a diameter [of 102mm], and a die length of 152mm in 150 micrometers of cell wall thickness, and cel consistency 62 cel / cm2. Although the mass per [in which 35.7% of porosity and A axial compression reinforcement are indicated to be 210kg/cm2 (20.6MPa), and include cell space] support volume is unstated, by count from a cel consistency, and cell wall thickness and cordierite true specific gravity 2.52 It is indicated that the honeycomb structure object with which the mass per [including cell space] support volume becomes in 1. and 360g /was acquired.

[0006] On the other hand, the desirable value is indicated by SAE Technical Paper Series 900614 about the cellular structure of a honeycomb structure object, bulk density, and porosity. For example, when cel consistencies are 400 cels / in2 (62 cels / cm2), rib thickness is 6mil (152 micrometers), and 35% and a cel consistency are [400 cels / in2 (62 cels / cm2), and rib thickness of bulk density] 5mil (127 micrometers) as for 0.43 g/cm3 (430g/(1.)) and porosity, bulk density is indicated to be 0.36 g/cm3 (360g/(1.)), and porosity is indicated to be 28%.

[0007]
[Problem(s) to be Solved by the Invention] In order to raise the quick warming of a catalytic converter, the heat capacity of the support for ceramic honeycomb structure catalysts can be reduced by making thin thickness of the cell wall for forming the cell space of the support for ceramic honeycomb structure catalysts, and porosity, i.e., a raise in porosity, is effective at one side for the support nature of the catalyst matter. However, since the mechanical strength of a cell wall falls, when the porosity of a cell wall is made high, and a cell wall is made thin, there is a problem that porosity cannot be made high.

[0008] Although invention currently indicated by aforementioned JP,4-70053,B is a thin wall, and has A axial compression reinforcement more than 200kg/cm2 (19.6MPa) and the mechanical strength has, since it is a thin wall, in order to satisfy said mechanical strength, porosity is made into 30% or less, and there is a problem that heat capacity is large and that quick warming is low.

[0009] Moreover, although invention of a publication has A axial compression reinforcement more than 210kg/cm2 (20.6MPa) in JP,6-69534,B, and it has the mechanical strength, and exceeds 30% and has 42% or less of porosity, cell wall thickness is about 150 micrometers, and has the problem which is large and quick warming does not have. [of heat capacity]

[0010] Although the relation between the cel consistency of a honeycomb structure object, wall thickness, bulk density, and porosity is indicated by SAE Technical Paper Series 900614, when cell wall thickness is made thin, porosity is decreasing to it and there is a problem which heat capacity has and quick warming does not have in it. [large]

[0011] Thus, the conventional honeycomb structure object raised the quick warming of a catalytic converter, i.e., in order to reduce the heat capacity of a honeycomb structure object, the cell wall was made to form into a thin wall, or porosity was made high, but sufficient reinforcement was not obtained when it was made such. That is, the formation of a thin wall of a cell wall, a raise in porosity, and implementation of the support for ceramic honeycomb structure catalysts with sufficient reinforcement are mutually recognized as a rate rebellion-problem of two. When the porosity of a cell wall is especially made high the support disposition top of a catalyst for a heat-capacity fall, the mechanical strength of the support for ceramic honeycomb structure catalysts falls.

[0012] The purpose of this invention is gathering the porosity of a cell wall, and it is to offer the support for ceramic honeycomb structure catalysts which has sufficient mechanical strength while heat capacity falls and quick warming improves by acquiring a more nearly lightweight honeycomb structure object, even if it is the same cell wall thickness. That is, since A axial compression reinforcement which can give the reinforcement of sufficient honeycomb structure object is maintained, it has high porosity, even if a cell wall is formed into a thin wall, and even if the bulk density which is the mass per volume of the support for ceramic honeycomb structure catalysts including cell space is a low honeycomb structure object, it is in offering the quick-warming support

for nature of cordierite ceramic honeycomb structure catalysts and its quick-warming manufacture approach of a high low-fever capacity.
[0013]
[Means for Solving the Problem] this invention persons paid their attention to the pore of a ceramic honeycomb, in order to offer the support for ceramic honeycomb structure catalysts which has sufficient mechanical strength, while heat capacity falls by acquiring a more nearly lightweight honeycomb structure object and quick warming improves, even if it is the same cell wall thickness by gathering the porosity of a cell wall. And when making the diameter of the pore formed in a ceramic honeycomb, and pore volume limit to the specific range, it found out that high porosity and high intensity could be attained. And in the manufacture approach, it found out that you were made to limit the diameter of the pore formed in a ceramic honeycomb by adjusting appropriately the programming rate of the temperature field to which the solid phase reaction at the time of baking goes, and pore volume to the specific range. Thereby, it was as high as 35% or more in the porosity of the support for honeycomb structure catalysts, and it became possible, it became clear that A axial compression reinforcement more than fixed was obtained further, and lightweight-izing mass per [including cell space] support volume in 1. and 400g /or less also reached this invention.
[0014] This invention is the honeycomb structure object with which the principal component of a crystal phase consists of a nature ceramic of cordierite concretely. The total pore volume of pore with a diameter of 0.5-2 micrometers 30% or more of total pore volume The total pore volume of pore with a diameter of 5-10 micrometers is [the total pore volume of pore with a total pore volume / 20% or less of / and a diameter of 10 micrometers or more] 30% or less of total pore volume. Porosity is the support for nature of cordierite ceramic honeycomb structure catalysts whose mass per [in which A axial compression reinforcement includes 18 or more MPas and cell space] support volume is 400g/l. or less 35% or more. And in case the manufacture approach for obtaining said support carries out mixed kneading and calcinates a cordierite-ized raw material after extrusion molding on a honeycomb structure object, it is characterized by making a programming rate later than the programming rate [within the area] till then more than 50 degrees C / Hr in the middle of the temperature up in the temperature field to which the solid phase reaction of a honeycomb structure object goes. Furthermore, in about 1200-1300 degrees C which is the temperature field to which this solid phase reaction goes, it is more preferably characterized by making the programming rate of about 1250 to 1300 between later than the programming rate for about 1200-1250 degrees C more than 50 degrees C / Hr.
[0015] In this invention, although porosity is maintaining 35% or more and high level That the support for ceramic honeycomb structure catalysts of the low-fever capacity whose mass per [which has high A axial compression reinforcement of 18 or more MPas, and includes cell space] support volume is 400g/l. or less is obtained It is because the optimal programming rate was found out in the temperature field to which solid phase reaction goes at the time of baking the manufacture approach of this support for honeycomb structure catalysts, especially as above-mentioned.
[0016] In the support for nature of cordierite ceramic honeycomb structure catalysts of this invention, the reason for having carried out mass per [including cell space] support volume in 400g/l. or less is as follows. It is because that temperature rise becomes late and quick warming is inferior, when the increment in the heat capacity of the support for ceramic honeycomb structure catalysts is caused and this support for honeycomb structure catalysts is heated by exhaust gas when 1. is exceeded in 400g /.
[0017] Moreover, in this invention, it is because A axial compression reinforcement to which having set A axial compression reinforcement (compressive strength of the direction of passage of the support for honeycomb structure catalysts) to 18 or more MPas can bear a severe service condition at the time of use of the support for honeycomb structure catalysts needs 18 or more MPas. It is because support reinforcement sufficient as support for honeycomb structure catalysts in less than 18 MPas is not obtained, but A axial compression reinforcement cannot finish bearing the stress generated at the time of canning which makes the support for honeycomb structure catalysts hold in a case, or the use after canning and may be damaged. Moreover, if the thermal shock resistance of the support for honeycomb structure catalysts is related and A axial compression reinforcement becomes high, the resistance to a thermal shock will also become large and thermal shock resistance

of A axial compression reinforcement will also improve. For this reason, the support for honeycomb structure catalysts which also has the thermal shock resistance which is not damaged according to the sudden temperature up according that A axial compression reinforcement is 18 or more MPas to exhaust gas, either can be obtained.

[0018] While catalyst support nature falls, in this invention, the porosity of the support for honeycomb structure catalysts is made into 35% or more at less than 35% of porosity because the increment in the heat capacity of the support for honeycomb structure catalysts is caused and quick warming falls. In addition, in this invention, desirable porosity is 38% or more, and when the upper limit takes into consideration the fall of A axial compression reinforcement, it is desirable [porosity] to make it to 50% or less.

[0019] In this invention, the reason which limited the total pore volume of pore with a diameter of 0.5-2 micrometers with 30% or more of total pore volume is that A axial compression reinforcement of the support for nature of cordierite ceramic honeycomb structure catalysts falls since the total pore volume of pore with a diameter of 2 micrometers or more becomes large substantially at 35% or more of porosity with the total pore volume of pore with a diameter of 0.5-2 micrometers being less than 30% of total pore volume. Although the support for ceramic honeycomb structure catalysts of this invention had porosity as high as 35% or more by having made the total pore volume of detailed pore with a diameter of 0.5-2 micrometers become 30% or more of total pore volume, it also became possible to lightweight-ize mass per [in which A axial compression reinforcement improves to 18 or more MPas, and moreover includes cell space] support volume in l. and 400g /or less.

[0020] And 20% or less of total pore volume and the limited reason the total pore volume of pore with a diameter of 5-10 micrometers If the total pore volume of pore with a diameter of 5-10 micrometers becomes larger [total pore volume] than 20% It is because a pore's with a diameter of 5-'s10 micrometers which can serve as origin's of destruction of support for honeycomb structure catalysts existence probability becomes high, a pore's with a diameter of 5 micrometers or more existence probability also becomes high at the maximum stress generating section and the mechanical strength of the support for nature of cordierite ceramic honeycomb structure catalysts falls as a result.

[0021] Furthermore, 30% or less of total pore volume and the limited reason the total pore volume of pore with a diameter of 10 micrometers or more A pore's with a diameter of 10 micrometers or more which can serve as origin's of destruction of support if total pore volume's of pore with a diameter of 10 micrometers becomes larger [total pore volume] than 30%'s existence probability becomes high. It is because the support matter advances into that the mechanical strength of the support for nature of cordierite ceramic honeycomb structure catalysts falls, and coincidence to the interior of a cell wall and the thermal shock resistance of support falls to them.

[0022] In the manufacture approach of the support for nature of cordierite ceramic honeycomb structure catalysts of this invention, the reason for making a programming rate late more than 50 degrees C / Hr in the middle of the temperature up in the temperature field to which solid phase reaction goes at the baking process after extrusion molding of this support for ceramic honeycomb structure catalysts depends on having found out that the programming rate in the temperature field to which solid phase reaction goes contributed to the coefficient of thermal expansion of the support for nature of cordierite ceramic honeycomb structure catalysts, porosity, and pore distribution. That is, the honeycomb structure baking object to which the heat shrink was carried out, eburnation progressed rapidly, and a raw material grain spacing became small by baking before the temperature field to which solid phase reaction goes is because low-fever expansion and high porosity are obtained in the process which promotes cordierite-ization in the liquid-phase reaction-temperature field which is a main reaction by making the programming rate of the anaphase of this temperature field later than the programming rate in the early stages of this temperature field more than 50 degrees C / Hr into the temperature field to which solid phase reaction goes. Namely, by making a programming rate later than the rate in early stages of the said field more than 50 degrees C / Hr from the temperature order from which expansion begins in the temperature field to which solid phase reaction goes In order that eburnation may progress slowly, with the condition maintained of becoming low-fever expansion and high porosity by rapid rate fall, in the liquid phase reaction process which is a subsequent main reaction Pore with a diameter of 5 micrometers or more is

divided, detailed pore with a diameter of 0.5-2 micrometers increases, and the total pore volume of the pore which is this diameter of 0.5-2 micrometers can occupy 30% or more of total pore volume.
[0023] It is [that the temperature field to which solid phase reaction goes preferably here should just be 1200-1300 degrees C] good to make the programming rate during 1250-1300 degrees C of this temperature field anaphase later than the programming rate for initial 1200-1250 degrees C more than 50 degrees C / Hr. The same effectiveness can be acquired, although there is a difference of effectiveness if it performs that not a strict value but some difference may arise, and the temperature of 1250 degrees C of this boundary line lowers a programming rate in this temperature requirement, although the boundary line of the first stage and the anaphase of a temperature field indicated it as 1250 degrees C.
[0024]
[Embodiment of the Invention] Hereafter, the example of this invention is explained.
(Example 1) It blended at a rate as these indicate to Table 1 that becomes a cordierite presentation, using a kaolin, a temporary-quenching kaolin, talc, an alumina, an aluminum hydroxide, and a silica as raw material powder.
[0025]
[Table 1]

セラミック原料	化 学 組 成				(質量%)			平均粒径 (μm)	配合比 (質量%)
	SiO₂	Al₂O₃	MgO	CaO+Na₂O+K₂O	TiO₂	Fe₂O₃	Ig.Loss		
タルク	60.0	1.0	32	0.20	—	1.10	5.70	9.0	41.0
アルミナ	—	99.8	—	0.04	—	—	0.16	5.5	15.5
カオリン	44.6	38.3	0.03	0.31	0.79	0.30	15.66	3.5	19.0
仮焼カオリン	52.6	44.4	0.2	0.45	1.59	0.40	0.36	3.0	11.0
水酸化アルミニウム	—	65.1	—	—	—	0.01	34.99	1.8	7.5
シリカ	99.3	0.1	—	0.02	0.02	0.03	0.53	9.2	6.0

[0026] Added methyl cellulose and lubricant as a binder to the raw material powder blended with the rate shown in Table 1, after adding, kneading and carrying out extrusion molding of the water, it was made to dry, and the honeycomb structure desiccation object of a configuration as shown in drawing 3 was manufactured. the thickness of a cell wall of the configuration of this honeycomb structure desiccation object is [square / 1] sentimental 150 micrometers -- per -- the number of cels -- the square cel configuration of 62 pieces -- having -- the diameter of 105mm, and die length of 118mm -- it was presupposed that it is cylindrical. This honeycomb structure desiccation object was loaded on the shelf board of a batch type firing furnace, and was calcinated, and the support for nature of cordierite ceramic honeycomb structure catalysts was obtained. The programming rate which is 1200-1300 degrees C which is the temperature field to which solid phase reaction goes at the time of this baking experimented in what kind of effect it has to the pore and reinforcement of a honeycomb structure object. This experimental result is shown in Table 2. When the programming rate in a 1200-1250 degrees C temperature region and a 1250-1300-degree C temperature region is changed and is calcinated, Table 2 The rate of occupying to the total pore volume and its total pore volume of the pore total pore volume, porosity, and whose diameter are 0.5-2 micrometers, The rate of occupying to the total pore volume and its total pore volume of being [a diameter / 5-10 micrometers] pore, The result of having measured the mass per [including the rate, A axial compression reinforcement, and cell space which are occupied to the total pore volume and its total pore volume of the pore whose diameter is 10 micrometers or more] support volume (g/l and l being a liter) is shown. Moreover, in this experiment, the desired value of A axial compression reinforcement is set up with 18 or more MPas, makes 18 or more MPas improper (it expresses as x mark) in good (it expresses as O mark), and less than 18 MPas, and shows this evaluation result to the on-the-strength evaluation column of Table 2. In addition, measurement of porosity and pore distribution was measured with the method of mercury penetration.
[0027]
[Table 2]

試験 No.	昇温速度(℃/Hr) 1200～1250℃	1250～1300℃	全細孔容積 (ml/g)	気孔率 (%)	細孔直径0.5～2μm 総細孔容積 (ml/g)	全細孔容積に占る割合(%)	細孔直径5～10μm 総細孔容積 (ml/g)	全細孔容積に占る割合(%)	細孔直径10μm以上 総細孔容積 (ml/g)	全細孔容積に占る割合(%)	A軸圧縮強度 (MPa)	担体容積当り貫量 (g/l)	強度評価	備考
1	66	15	0.223	37.8	0.068	30.5	0.044	19.7	0.053	23.8	19.9	392	○	本発明
2	66	15	0.216	37.9	0.066	30.6	0.036	16.7	0.056	25.9	18.9	388	○	本発明
3	66	15	0.219	38.4	0.069	31.5	0.037	16.9	0.056	25.6	18.8	382	○	本発明
4	100	15	0.235	38.6	0.074	31.5	0.040	17.0	0.057	24.3	20.7	376	○	本発明
5	100	15	0.234	38.3	0.073	31.2	0.041	17.5	0.052	22.2	19.3	375	○	本発明
6	100	15	0.233	39.3	0.076	32.6	0.040	17.2	0.051	21.9	19.7	370	○	本発明
7	100	15	0.227	39.0	0.081	35.7	0.033	14.5	0.047	20.7	18.9	372	○	本発明
8	50	7.5	0.212	35.7	0.017	8.0	0.081	38.2	0.087	41.0	18.2	420	○	比較例
9	50	7.5	0.212	36.8	0.028	13.2	0.071	33.5	0.078	36.8	18.2	408	○	比較例
10	50	7.5	0.221	37.9	0.023	10.4	0.078	35.3	0.081	36.7	17.0	389	×	比較例
11	50	7.5	0.226	38.6	0.024	10.6	0.085	37.6	0.075	33.2	17.2	383	×	比較例
12	50	7.5	0.233	40.0	0.026	11.2	0.084	36.1	0.090	38.6	15.8	364	×	比較例
13	120	120	0.215	35.6	0.028	13.0	0.078	36.3	0.052	24.2	20.2	422	○	従来例
14	120	120	0.221	36.5	0.025	11.3	0.088	39.8	0.059	26.7	19.0	416	○	従来例
15	120	120	0.223	36.5	0.025	11.2	0.081	36.3	0.074	33.2	19.1	412	○	従来例
16	120	120	0.228	37.3	0.017	7.5	0.100	43.9	0.063	27.6	17.2	395	×	従来例
17	120	120	0.233	38.5	0.022	9.4	0.089	38.2	0.070	30.0	16.3	378	×	従来例

（注）(ml／g)、(g／l)のlはリットルを示す

[0028] So that clearly from Table 2 the programming rate in a 1200-1300-degree C temperature field In trial No.1-7 which are the example of this invention which made late this field anaphase (1250-1300 degrees C) more than 50 degrees C / Hr to the early stages of the said field (1200-1250 degrees C) As for porosity, the support for nature of cordierite ceramic honeycomb structure catalysts with which 400g [l.] /or less and A axial compression reinforcement are [the mass per / which includes cell space 35% or more (all are 37.8% or more) / support volume] satisfied of 18 or more MPas was obtained. Moreover, as for pore volume, 30% or less of support for nature of cordierite ceramic honeycomb structure catalysts of total pore volume was obtained [the pore whose pores with a diameter of 0.5-2 micrometers are 30% or more of total pore volume, and the diameter of 5-10 micrometers] for pore with a diameter of 10 micrometers or more 20% or less of total pore volume.
[0029] In on the other hand, trial No.8-12 which are the example of a comparison which set the programming rate of 1200-1250 degrees C at the time of baking to 50 degrees C/Hr, and set the programming rate of 1250-1300 degrees C to 7.5 degrees C/Hr and a 1200-1300-degree C temperature field In trial No.13-17 which are the conventional example which set the programming rate to 120 degrees C/Hr The support for nature of cordierite ceramic honeycomb structure catalysts with which 400g [l.] /or less and A axial compression reinforcement are [porosity / the mass per support volume] satisfied of all of 18 or more MPas**s 35% or more was not obtained. It sets for the example of these comparisons, and the conventional example especially. The rate that the total pore volume of pore with a diameter of 0.5-2 micrometers occupies to total pore volume becomes low with 7.5 - 13.2%. Moreover, the rate that the total pore volume of pore with a diameter of 5-10 micrometers occupies to total pore volume becomes high with 33.5 - 43.9%. It is guessed for the mass per [including cell space] support volume 35% or more that porosity is the reason the support for nature of cordierite ceramic honeycomb structure catalysts with which 400g [l.] /or less and A axial compression reinforcement are satisfied of all of 18 or more MPas was not obtained as this is the above. The relation of the diameter of the pore of the support for nature of cordierite ceramic honeycomb structure catalysts and accumulation pore volume which were obtained with the programming rate of trial No.4 (example of this invention) and trial No.14 (conventional example) is shown in drawing 1 . Drawing 1 is a graph which shows the relation between the diameter (logarithmic scale) of pore, and accumulation pore volume, and, as for trial No.4 (example of this invention), and Curve B, Curve A shows trial No.14 (conventional example).
[0030] In the support for nature of cordierite ceramic honeycomb structure catalysts which has the thin wall whose thickness of a cell wall is 150 micrometers from the above-mentioned example 1 A programming rate is changed in a 1200-1300-degree C burning-temperature field, and pore of the support for nature of cordierite ceramic honeycomb structure catalysts is made detailed, Namely, in the temperature field which is about 1200-1300 degrees C which is in the temperature field to which the solid phase reaction of the support for nature of cordierite ceramic honeycomb structure catalysts goes The programming rate of 1250-1300 degrees C which it is in the middle of a temperature up by making it later than a 1200-1250-degree C field more than 50 degrees C / Hr Porosity was as high as

35% or more, and though it was lightweight, it became clear that the support for nature of cordierite ceramic honeycomb structure catalysts without the thing whose mass per [which includes cell space further] support volume cannot be found in the former 400g [/l.] or less and for which A axial compression reinforcement is reduced is obtained.

[0031] (Example 2) As a catalyst, in an assembly and this honeycomb support, exhaust gas was passed and the support for nature of cordierite ceramic honeycomb structure catalysts calcinated and obtained with the programming rate shown in trial No.2 (example of this invention) of Table 2, trial No.4 (example of this invention), and trial No.14 (conventional example) was actually measured about quick warming. Drawing 2 is a graph which shows the relation between the exhaust gas temperature of the inlet port of a catalyst, and an outlet which it is as a result of [this] measurement, and elapsed time. In drawing 2 , so that clearly from the curve which shows change of the outlet temperature of the exhaust gas of the outlet of a catalyst trial No.14 which are the conventional example after about 30-second progress, and trial No. which is an example of this invention -- 2 and 4 It became clear that the support for nature of cordierite ceramic honeycomb structure catalysts which acquired the time amount which reaches about 200-250 degrees C which is the temperature which a difference begins to produce in quick warming and a catalyst begins to activate by the baking approach of this invention is shortened for about 8 seconds as compared with the support obtained by the conventional baking approach. Thus, since mass per [including that the rate of pore with as detailed pore with a diameter of 0.5-2 micrometers as 30% or more of total pore volume is high and cell space] support volume was lightweight-ized in l. and 400g /or less, it is guessed that the reason whose quick warming improves in the example of this invention is what is depended on heat capacity having fallen.

[0032] In explanation of the gestalt of operation of above-mentioned this invention explained above, although the cell space of the support for ceramic honeycomb structure catalysts explained the square cel configuration, this invention is applicable also to a hexagon besides a square cel configuration, and the other configurations of arbitration. Moreover, the cross-section configuration of the support for nature of cordierite ceramic honeycomb structure catalysts of this invention is applicable not only to a round shape but elliptical.

[0033]

[Effect of the Invention] Since mass per [in which catalyst support nature is good for, and includes cell space since porosity is as high as 35% or more] support volume is lightweight-ized in l. and 400g /according to this invention, heat capacity is small, quick warming is good, and since it moreover has high A axial compression reinforcement, the support for nature of cordierite ceramic honeycomb structure catalysts which has high support reinforcement can be obtained. For this reason, the time amount to catalytic-activity-izing at the time of a cold start can be shortened, moreover, also to the pressure by Canning, and the thermal stress by the thermal shock, it is strong and the very reliable support for nature of cordierite ceramic honeycomb structure catalysts can be offered.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the graph which shows the relation of the pore diameter of nature of cordierite ceramic honeycomb structure catalyst support and accumulating-totals pore volume which were manufactured by the manufacture approach of this invention, and the manufacture approach of the conventional example.
[Drawing 2] In the nature of cordierite ceramic honeycomb structure catalyst support of this invention and the conventional example, it is the graph which shows the relation between the outlet temperature of the exhaust gas at the time of a cold start, and elapsed time.
[Drawing 3] (a) is drawing showing the appearance of nature of cordierite ceramic honeycomb structure catalyst support, and (b) is the important section enlarged drawing of the cell space section of drawing 3 (a).
[Description of Notations]
1: Support for nature of cordierite ceramic honeycomb structure catalysts
2: Cell space
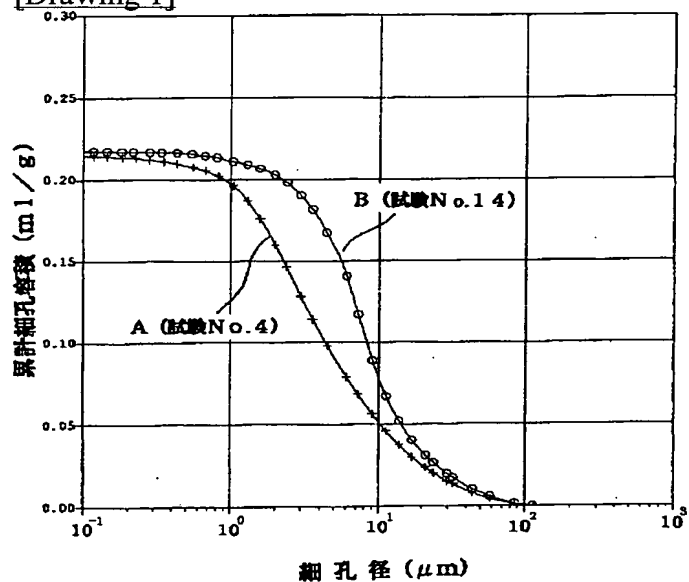3: Cell wall
4: Peripheral wall

[Translation done.]

* NOTICES *

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damages caused by the use of this translation.
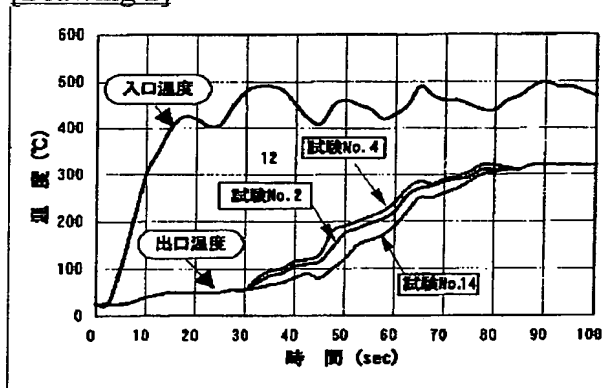
1.This document has been translated by computer. So the translation may not reflect the original
precisely.
2.**** shows the word which can not be translated.
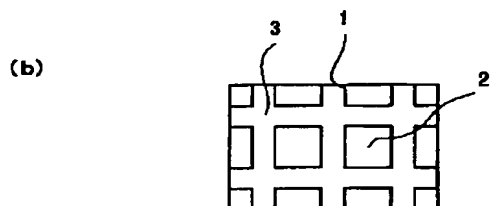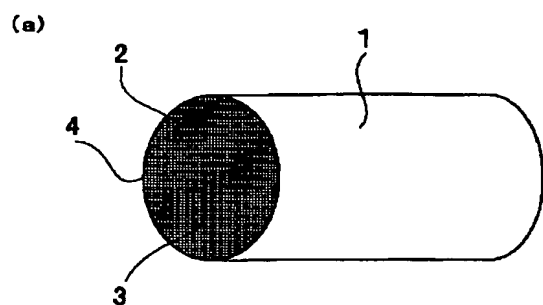3.In the drawings, any words are not translated.

DRAWINGS

[Drawing 1]

[Drawing 2]

[Drawing 3]

(a)

(b)

[Translation done.]

(51)Int.Cl.⁷	識別記号	FI	テーマコード゛(参考)
B01J　35/04	301	B01J　35/04　　301K	4G030
32/00		32/00	4G069
C04B　35/195		C04B　35/16　　　A	

審査請求　有　　請求項の数3　OL　（全 7 頁）

(54)【発明の名称】　コージェライト質セラミックハニカム構造触媒用担体及びその製造方法

(57)【要約】

【課題】　同じセル壁厚であっても、セル壁の気孔率を上げることで、より軽量なハニカム構造体を得ることにより、速熱性が向上し、十分な機械的強度を有するセラミックハニカム構造触媒用担体を得る。

【解決手段】　直径0.5～2μmの細孔の総細孔容積が全細孔容積の30％以上、直径5～10μmの細孔の総細孔容積が全細孔容積の20％以下、直径10μm以上の細孔の総細孔容積が全細孔容積の30％以下であり、気孔率が35％以上、A軸圧縮強度が18MPa以上、かつセル空間を含む担体容積あたりの質量が400g／リットル以下のコージェライト質セラミックハニカム構造触媒用担体とする。

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【特許請求の範囲】

【請求項１】　結晶相の主成分がコージェライト質セラミックからなるハニカム構造体で、直径０．５～２μｍの細孔の総細孔容積が全細孔容積の３０％以上、直径５～１０μｍの細孔の総細孔容積が全細孔容積の２０％以下、直径１０μｍ以上の細孔の総細孔容積が全細孔容積の３０％以下であり、気孔率が３５％以上、Ａ軸圧縮強度が１８ＭＰａ以上、かつセル空間を含む担体容積あたりの質量が４００ｇ／リットル以下であることを特徴とするコージェライト質セラミックハニカム構造触媒用担体。

【請求項２】　コージェライト化原料を混合混練してハニカム構造体に押し出し成形後、焼成するコージェライト質セラミックハニカム構造触媒用担体の製造方法において、前記ハニカム構造体の固相反応が進む温度領域内の昇温途中で、昇温速度を同域内のそれまでの昇温速度より５０℃／Ｈｒ以上遅くすることを特徴とするコージェライト質セラミックハニカム構造触媒用担体の製造方法。

【請求項３】　ハニカム構造体の固相反応が進む温度領域である約１２００～１３００℃において、１２５０～１３００℃間の昇温速度を１２００～１２５０℃間の昇温速度より５０℃／Ｈｒ以上遅くすることを特徴とする請求項２に記載のコージェライト質セラミックハニカム構造触媒用担体の製造方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、排ガス浄化装置に用いられるコージェライト質セラミックハニカム構造触媒用担体及びその製造方法に関するものである。

【０００２】

【従来の技術】最近の排ガス規制強化による排出総量低減の要請に伴い、図３に示すようなコージェライト質のセラミックハニカム構造触媒用担体１を用いた排ガス浄化装置には、従来以上に卓越した排ガス浄化性能の実現が期待されている。コージェライト質を主成分とするセラミックハニカム構造触媒用担体１の組成は、主にＳｉＯ₂、Ａｌ₂Ｏ₃、ＭｇＯから構成されている。このようなセラミックハニカム構造触媒用担体１を用いた排ガス浄化装置においては、冷間からエンジンをスタートした状態であるコールドスタート時は触媒がまだ暖まっていないために活性化しておらず、排ガスの浄化効率が著しく低い。このため、コールドスタート時における触媒の早期活性化が排ガス規制をクリアーするための最重要課題とされている。このような課題を解決するために、最近では、セラミックハニカム構造触媒用担体１のセル空間２を形成するためのセル壁３の厚みを薄くすること、または、セル空間を含む担体容積あたりの質量即ち嵩密度を小さくすることにより、このセラミックハニカム構造触媒用担体１の熱容量を低下させて、触媒の速熱

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性を高める技術が採用されている。

【０００３】また、触媒コンバーターの速熱性を高めるには高気孔率化による嵩密度の低下も有効であり、さらに活性アルミナや白金等の触媒物質を多量に担持するためにも、セラミックハニカム構造触媒用担体１を多孔性即ち、高気孔率にすることは重要な特性の一つになっている。

【０００４】特公平４－７００５３号公報には、薄壁でしかも強度特性を満足できる低気孔率レベルを有する低熱膨張のハニカム構造触媒用担体の提供を目的として、気孔率が３０％以下でありハニカム構造体の流路方向の圧縮強度（Ａ軸圧縮強度）が２００ｋｇ／ｃｍ²（１９．６ＭＰａ）以上のコージェライトハニカム構造触媒用担体が開示されている。同公報の実施例中試験Ｎｏ．６には、セル壁厚１０２μｍ、セル密度９３セル／ｃｍ²のセル構造の場合、気孔率２５．４％、Ａ軸圧縮強度が２６３ｋｇ／ｃｍ²（２５．８ＭＰａ）と記載され、セル空間を含む担体容積あたりの質量は記載がないが、セル密度とセル壁厚、コージェライト真比重２．５２から計算により、セル空間を含む担体容積あたりの質量が３５０ｇ／リットルとなるコージェライトハニカム構造触媒用担体が記載されている。そして、ハニカム構造触媒用担体の実使用用において、過酷な使用条件でも耐えることができるＡ軸圧縮強度が１９．６ＭＰａ以上のレベルを示す触媒担体のセル構造を設計することが可能になったと記載されている。

【０００５】また、特公平６－６９５３４号公報には、コージェライト担体よりも熱膨張係数の大きい活性アルミナ及び他の触媒成分の担持により耐熱衝撃性劣化の少ないハニカム構造触媒担体として使用するのに好適なコージェライト構造体の提供を目的として、ハニカム構造体の気孔率が３０％を超え４２％以下であって、直径０．５～５μｍの細孔の総細孔容積が全細孔容積の７０％以上で、直径１０μｍ以上の細孔容積が全細孔容積の１０％以下であるコージェライトハニカム構造体が開示されている。同公報の実施例中試験Ｎｏ．３には、セル壁厚１５０μｍ、セル密度６２セル／ｃｍ²で直径１０２ｍｍ、長さ１５２ｍｍの円筒形コージェライトハニカム構造触媒担体において、気孔率３５．７％、Ａ軸圧縮強度が２１０ｋｇ／ｃｍ²（２０．６ＭＰａ）と記載され、セル空間を含む担体容積あたりの質量は記載がないが、セル密度とセル壁厚、コージェライト真比重２．５２から計算により、セル空間を含む担体容積あたりの質量が３６０ｇ／リットルとなるハニカム構造体が得られたことが記載されている。

【０００６】一方、SAE Technical Paper Series ９００６１４には、ハニカム構造体のセル構造、嵩密度、気孔率について望ましい値が記載されている。例えば、セル密度が４００セル／in²（６２セル／ｃｍ²）、リブ厚が６ｍｉｌ（１５２μｍ）の場合、嵩密度は０．４３ｇ

／cm³（４３０ｇ／リットル）、気孔率は３５％、また
セル密度が４００セル／in²（６２セル／cm²）、リ
ブ厚が５mil（１２７μm）の場合、嵩密度は０．３６
ｇ／cm³（３６０ｇ／リットル）、気孔率は２８％と記
載されている。

【０００７】
【発明が解決しようとする課題】触媒コンバーターの速
熱性を高める為、セラミックハニカム構造触媒用担体の
セル空間を形成するためのセル壁の厚みを薄くすること
で、セラミックハニカム構造触媒用担体の熱容量を低下
させることができ、一方で触媒物質の担持性の為には多
孔性即ち高気孔率化が有効である。しかし、セル壁の気
孔率を高くした場合、セル壁の機械的強度が低下するの
でセル壁を薄くすると気孔率を高くできないという問題
がある。

【０００８】前記の特公平４－７００５３号公報に開示
されている発明は、薄壁でかつ２００kg／cm²（１
９．６MPa）以上のA軸圧縮強度があり、機械的強度
は有しているが、薄壁である為、前記機械的強度を満足
させる為に気孔率を３０％以下としており、熱容量が大
きく速熱性が低い問題がある。

【０００９】また特公平６－６９５３４号公報に記載の
発明は、２１０kg／cm²（２０．６MPa）以上の
A軸圧縮強度があり、機械的強度を有しており、３０％
を超え４２％以下の気孔率を有しているが、セル壁厚は
１５０μm程度であり熱容量が大きく速熱性は十分では
ない問題がある。

【００１０】SAE Technical Paper Series ９００６１
４には、ハニカム構造体のセル密度、壁厚、嵩密度、気
孔率との関係について記載されているが、セル壁厚を薄
くすると、気孔率は減少しており、熱容量は大きく速熱
性は十分でない問題がある。

【００１１】このように、従来のハニカム構造体は、触
媒コンバータの速熱性を高めるすなわち、ハニカム構造
体の熱容量を低下させるためには、セル壁を薄壁化させ
たり、気孔率を高くしたりしていたが、そのようにする
と十分な強度が得られなかった。つまり、セル壁の薄壁
化や高気孔率化と、十分な強度を持つセラミックハニカ
ム構造触媒用担体の実現とは、互いに二率背反的な問題
として認識されている。特に、触媒の担持性向上と熱容
量低下のためにセル壁の気孔率を高くした場合、セラミ
ックハニカム構造触媒用担体の機械的強度は低下する。

【００１２】本発明の目的は、セル壁の気孔率を上げる
ことで、同じセル壁厚であってもより軽量なハニカム構
造体を得ることにより、熱容量が低下し、速熱性が向上
するとともに、十分な機械的強度を有するセラミックハ
ニカム構造触媒用担体を提供することにある。つまり、
十分なハニカム構造体の強度を与えることができるA軸
圧縮強度を維持することから、セル壁が薄壁化されても
高い気孔率を有し、セル空間を含むセラミックハニカム

構造触媒用担体の容積あたりの質量である嵩密度が低い
ハニカム構造体であっても、速熱性の高い低熱容量のコ
ージェライト質セラミックハニカム構造触媒用担体及び
その製造方法を提供することにある。

【００１３】
【課題を解決するための手段】本発明者らは、セル壁の
気孔率を上げることにより、同じセル壁厚であってもよ
り軽量なハニカム構造体を得ることで熱容量が低下し、
速熱性が向上するとともに、十分な機械的強度を有する
セラミックハニカム構造触媒用担体を提供するために
は、セラミックハニカムの細孔に着目した。そして、セ
ラミックハニカムに形成される細孔の直径、及び細孔容
積を特定範囲に限定させれば、高気孔率かつ高強度を達
成できることを見出した。そして、その製造方法におい
て、焼成時の固相反応が進む温度領域の昇温速度を適切
に調整することでセラミックハニカムに形成される細孔
の直径、及び細孔容積を特定範囲に限定させられること
を見出した。これにより、ハニカム構造触媒用担体の気
孔率を３５％以上と高く、かつセル空間を含む担体容積
あたりの質量を４００ｇ／リットル以下と軽量化するこ
とも可能になり、さらに一定以上のA軸圧縮強度が得ら
れることが判明し、本発明に到達したのである。

【００１４】具体的に本発明は、結晶相の主成分がコー
ジェライト質セラミックからなるハニカム構造体で、直
径０．５～２μmの細孔の総細孔容積が全細孔容積の３
０％以上、直径５～１０μmの細孔の総細孔容積が全細
孔容積の２０％以下、直径１０μm以上の細孔の総細孔
容積が全細孔容積の３０％以下であり、気孔率が３５％
以上、A軸圧縮強度が１８MPa以上、かつセル空間を
含む担体容積あたりの質量が４００ｇ／リットル以下で
あるコージェライト質セラミックハニカム構造触媒用担
体である。そして、前記担体を得るための製造方法は、
コージェライト化原料を混合混練してハニカム構造体に
押し出し成形後焼成する際に、ハニカム構造体の固相反
応が進む温度領域内の昇温途中で、昇温速度を同域内の
それまでの昇温速度より５０℃／Hr以上遅くすること
を特徴とする。さらに、より好ましくは、この固相反応
が進む温度領域である約１２００～１３００℃におい
て、約１２５０～１３００間の昇温速度を約１２００～
１２５０℃間の昇温速度より５０℃／Hr以上遅くする
ことを特徴とする。

【００１５】本発明において、気孔率が３５％以上と高
いレベルを維持しているにもかかわらず、１８MPa以
上の高いA軸圧縮強度を有し、かつセル空間を含む担体
容積あたりの質量が４００ｇ／リットル以下である低熱
容量のセラミックハニカム構造触媒用担体が得られるの
は、このハニカム構造触媒用担体の製造方法、特に上記
の通り、焼成時に固相反応が進む温度領域内において、
最適な昇温速度を見出したことによる。

【００１６】本発明のコージェライト質セラミックハニ

カム構造触媒用担体において、セル空間を含む担体容積あたりの質量を４００ｇ／リットル以下とした理由は次の通りである。４００ｇ／リットルを超えると、セラミックハニカム構造触媒用担体の熱容量の増加を招き、このハニカム構造触媒用担体が排ガスにより加熱された時にその温度上昇が遅くなり、速熱性が劣るからである。

【００１７】また、本発明において、Ａ軸圧縮強度（ハニカム構造触媒用担体の流路方向の圧縮強度）を１８ＭＰａ以上としたのは、ハニカム構造触媒用担体の使用時においては、過酷な使用条件に耐えることのできるＡ軸圧縮強度は１８ＭＰａ以上を必要とするからである。Ａ軸圧縮強度が１８ＭＰａ未満では、ハニカム構造触媒用担体として十分な担体強度が得られず、ハニカム構造触媒用担体をケースに収容させるキャニング時、或いはキャニング後の使用時に発生する応力には耐えきれず、破損する場合があるからである。またＡ軸圧縮強度は、ハニカム構造触媒用担体の耐熱衝撃性とも関係があり、Ａ軸圧縮強度が高くなると熱衝撃に対する抵抗も大きくなり耐熱衝撃性も向上する。このため、Ａ軸圧縮強度が１８ＭＰａ以上であると、排ガスによる急昇温によっても破損しない耐熱衝撃性も有するハニカム構造触媒用担体を得ることができる。

【００１８】本発明において、ハニカム構造触媒用担体の気孔率を３５％以上とするのは、気孔率３５％未満では、触媒担持性が低下するとともに、ハニカム構造触媒用担体の熱容量の増加を招き速熱性が低下するからである。なお本発明において、望ましい気孔率は３８％以上であり、その上限値はＡ軸圧縮強度の低下を考慮すると気孔率は５０％以下にすることが好ましい。

【００１９】本発明において、直径０．５〜２μｍの細孔の総細孔容積を全細孔容積の３０％以上と限定した理由は、気孔率３５％以上で直径０．５〜２μｍの細孔の総細孔容積が全細孔容積の３０％未満であると実質的に直径２μｍ以上の細孔の総細孔容積が大きくなるため、コージェライト質セラミックハニカム構造触媒用担体のＡ軸圧縮強度が低下するからである。本発明のセラミックハニカム構造触媒用担体は、直径０．５〜２μｍの微細な細孔の総細孔容積を全細孔容積の３０％以上になるようにしたことにより、気孔率が３５％以上と高いにもかかわらずＡ軸圧縮強度が１８ＭＰａ以上に向上し、しかもセル空間を含む担体容積あたりの質量を４００ｇ／リットル以下と軽量化することも可能になったのである。

【００２０】そして、直径５〜１０μｍの細孔の総細孔容積を全細孔容積の２０％以下と限定した理由は、直径５〜１０μｍの細孔の総細孔容積が全細孔容積の２０％より大きくなると、ハニカム構造触媒用担体の破壊の起点となりうる直径５〜１０μｍの細孔の存在確率が高くなり、最大応力発生部に直径５μｍ以上の細孔の存在確率も高くなり、結果として、コージェライト質セラミッ

クハニカム構造触媒用担体の機械的強度が低下するからである。

【００２１】さらに、直径１０μｍ以上の細孔の総細孔容積を全細孔容積の３０％以下と限定した理由は、直径１０μｍの細孔の総細孔容積が全細孔容積の３０％より大きくなると担体の破壊の起点となりうる直径１０μｍ以上の細孔の存在確率が高くなり、コージェライト質セラミックハニカム構造触媒用担体の機械的強度が低下するのと同時に、担持物質がセル壁内部まで進入して担体の耐熱衝撃性が低下するからである。

【００２２】本発明のコージェライト質セラミックハニカム構造触媒用担体の製造方法において、このセラミックハニカム構造触媒用担体の押し出し成形後の焼成工程で、固相反応が進む温度領域内の昇温途中で昇温速度を５０℃／Ｈｒ以上遅くする理由は、固相反応が進む温度領域での昇温速度がコージェライト質セラミックスハニカム構造触媒用担体の熱膨張係数、気孔率ならびに細孔分布に寄与することを見出したことによる。すなわち、固相反応が進む温度領域内において、この温度領域の後期の昇温速度を、同温度領域の初期での昇温速度より５０℃／Ｈｒ以上遅くすることにより、固相反応が進む温度領域以前の焼成により、熱収縮して緻密化が急激に進んで原料粒子間隔が小さくなったハニカム構造焼成体は、主反応である液相反応温度領域で、コージェライト化を促進する過程で低熱膨張と高気孔率が得られるからである。すなわち、固相反応が進む温度領域において、膨張が始まる温度前後から昇温速度を同領域初期の速度よりも５０℃／Ｈｒ以上遅くすることにより、急激な速度低下により低熱膨張と高気孔率となる状態を維持したままゆっくりと緻密化が進むため、その後の主反応である液相反応過程で、直径５μｍ以上の細孔が分割されて、直径０．５〜２μｍの微細な細孔が増加し、この直径０．５〜２μｍの細孔の総細孔容積は全細孔容積の３０％以上を占めるようにすることができたものである。

【００２３】ここで、好ましくは固相反応が進む温度領域が１２００〜１３００℃であれば良く、この温度領域後期１２５０〜１３００℃間の昇温速度を、初期１２００〜１２５０℃間の昇温速度より５０℃／Ｈｒ以上遅くすると良い。温度領域の初期と後期の境目は１２５０℃と記載したが、この境目の温度１２５０℃は厳密な値ではなく、若干の差が生じてもよいし、この温度範囲内で昇温速度を下げることを行えば、効果の差はあるが、同様な効果を得ることができる。

【００２４】
【発明の実施の形態】以下、本発明の実施例について説明する。

（実施例１）原料粉末としてカオリン、仮焼カオリン、タルク、アルミナ、水酸化アルミニウム、及びシリカを用い、これらがコージェライト組成となるよう表１に示すような割合で配合した。

【００２５】　　　　　　　　　＊　＊【表１】

セラミック原料	化学組成　（質量%）							平均粒径(μm)	配合比(質量%)
	SiO₂	Al₂O₃	MgO	CaO+Na₂O+K₂O	TiO₂	Fe₂O₃	Ig.Loss		
タルク	60.0	1.0	32	0.20	—	1.10	5.70	9.0	41.0
アルミナ	—	99.8	—	0.04	—	—	0.16	5.5	15.5
カオリン	44.6	38.3	0.03	0.31	0.79	0.30	15.66	3.5	19.0
仮焼カオリン	52.8	44.4	0.2	0.45	1.59	0.40	0.36	3.0	11.0
水酸化アルミニウム	—	65.1	—	—	—	0.01	34.99	1.8	7.5
シリカ	99.3	0.1	—	0.02	0.02	0.03	0.53	9.2	6.0

【００２６】表１に示す割合に配合した原料粉末にバインダーとしてメチルセルロース、潤滑剤を添加し、水を加えて混練し、押し出し成形した後に乾燥させて、図３に示すような形状のハニカム構造乾燥体を製作した。このハニカム構造乾燥体の形状は、セル壁の厚みは１５０μm、１平方センチ当りのセル数６２個の四角セル形状を有し、直径１０５mm、長さ１１８mmの円柱状とした。このハニカム構造乾燥体をバッチ式焼成炉の棚板上に積載して焼成し、コージェライト質セラミックハニカム構造触媒用担体を得た。この焼成時において、固相反応が進む温度領域である１２００～１３００℃の昇温速度が、ハニカム構造体の細孔及び強度に対して如何なる影響を与えるかを実験した。この実験結果を表２に示している。表２は、１２００～１２５０℃の温度域、及び１２５０～１３００℃の温度域における昇温速度を変化※

※させて焼成したときに、全細孔容積、気孔率、直径が０．５～２μmである細孔の総細孔容積及びその全細孔容積に占める割合、直径が５～１０μmであるの細孔の総細孔容積及びその全細孔容積に占める割合、直径が１０μm以上である細孔の総細孔容積及びその全細孔容積に占める割合、A軸圧縮強度及びセル空間を含む担体容積当りの質量（ｇ／１、１はリットル）を測定した結果を示している。また、本実験ではA軸圧縮強度の目標値は１８ＭＰａ以上と設定し、１８ＭＰａ以上を良（○印で表示）、１８ＭＰａ未満を不可（×印で表示）とし、この評価結果を表２の強度評価欄に示している。なお、気孔率及び細孔分布の測定は水銀圧入法により測定した。

【００２７】

【表２】

試験No.	昇温速度(℃/Hr) 1200~1250℃	1250~1300℃	全細孔容積(ml/g)	気孔率(%)	細孔直径0.5~2μm 総細孔容積(ml/g)	全細孔容積に占める割合(%)	細孔直径5~10μm 総細孔容積(ml/g)	全細孔容積に占める割合(%)	細孔直径10μm以上 総細孔容積(ml/g)	全細孔容積に占める割合(%)	A軸圧縮強度(MPa)	担体容積当り質量(g/l)	強度評価	備考
1	66	15	0.223	37.8	0.068	30.5	0.044	19.7	0.053	23.8	19.9	392	○	本発明
2	66	15	0.216	37.9	0.066	30.6	0.036	16.7	0.056	25.9	18.9	388	○	本発明
3	66	15	0.219	38.4	0.069	31.5	0.037	16.9	0.056	25.6	18.8	382	○	本発明
4	100	15	0.235	38.6	0.074	31.5	0.040	17.0	0.057	24.3	20.7	376	○	本発明
5	100	15	0.234	38.3	0.073	31.2	0.041	17.5	0.052	22.2	19.3	375	○	本発明
6	100	15	0.233	39.3	0.076	32.6	0.040	17.2	0.051	21.9	19.7	370	○	本発明
7	100	15	0.227	39.0	0.081	35.7	0.033	14.5	0.047	20.7	18.9	372	○	本発明
8	50	7.5	0.212	35.7	0.017	8.0	0.081	38.2	0.087	41.0	18.2	420	○	比較例
9	50	7.5	0.212	36.8	0.028	13.2	0.071	33.5	0.078	36.8	18.2	408	○	比較例
10	50	7.5	0.221	37.9	0.023	10.4	0.078	35.3	0.081	36.7	17.0	389	×	比較例
11	50	7.5	0.226	38.6	0.024	10.6	0.085	37.6	0.075	33.2	17.2	383	×	比較例
12	50	7.5	0.233	40.0	0.026	11.2	0.084	36.1	0.090	38.6	15.8	364	×	比較例
13	120	120	0.215	35.8	0.028	13.0	0.078	36.3	0.052	24.2	20.2	422	○	従来例
14	120	120	0.221	36.5	0.025	11.3	0.088	39.8	0.059	26.7	19.0	416	○	従来例
15	120	120	0.223	36.5	0.025	11.2	0.081	36.3	0.074	33.2	19.1	412	○	従来例
16	120	120	0.228	37.3	0.017	7.5	0.100	43.9	0.063	27.6	17.2	395	×	従来例
17	120	120	0.233	38.5	0.022	9.4	0.089	38.2	0.070	30.0	16.3	378	×	従来例

（注)(ml／g)、(g／l)の l はリットルを示す

【００２８】表２から明らかなように、１２００～１３００℃の温度領域での昇温速度を、同領域初期（１２００～１２５０℃）に対して同領域後期（１２５０～１３００℃）を５０℃／Ｈｒ以上遅くした本発明例である試験Ｎｏ．１～７においては、気孔率は３５％以上（全てが３７．８％以上）、セル空間を含む担体容積当りの質量が４００ｇ／リットル以下、A軸圧縮強度が１８ＭＰａ以上、を満足するコージェライト質セラミックハニカム構造触媒用担体が得られた。また、細孔容積は、直径０．５～２μmの細孔が全細孔容積の３０％以上、直径５～１０μmの細孔が全細孔容積の２０％以下、直径１０μm以上の細孔が全細孔容積の３０％以下のコージェ

ライト質セラミックハニカム構造触媒用担体が得られた。

【００２９】これに対して、焼成時の１２００～１２５０℃の昇温速度を５０℃／Ｈｒにし、１２５０～１３００℃の昇温速度を７．５℃／Ｈｒとした比較例である試験Ｎｏ．８～１２、及び１２００～１３００℃の温度領域で、昇温速度を１２０℃／Ｈｒとした従来例である試験Ｎｏ．１３～１７においては、気孔率が３５％以上、担体容積当りの質量が４００ｇ／リットル以下、A軸圧縮強度が１８ＭＰａ以上、の全てを満足するコージェライト質セラミックハニカム構造触媒用担体は得られなかった。特に、これら比較例、及び従来例においては、直

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径０．５〜２μmの細孔の総細孔容積が全細孔容積に占める割合が７．５〜１３．２％と低くなり、また直径５〜１０μmの細孔の総細孔容積が全細孔容積に占める割合が３３．５〜４３．９％と高くなり、これが上記の通り気孔率が３５％以上、セル空間を含む担体容積当りの質量が４００ｇ／リットル以下、Ａ軸圧縮強度が１８ＭＰａ以上の全てを満足するコージェライト質セラミックハニカム構造触媒用担体が得られなかった理由と推測される。試験Ｎｏ．４（本発明例）と試験Ｎｏ．１４（従来例）の昇温速度で得たコージェライト質セラミックハニカム構造触媒用担体の細孔の直径と累積細孔容積との関係を図１に示す。図１は細孔の直径（対数目盛）と累積細孔容積との関係を示すグラフであり、曲線Ａは試験Ｎｏ．４（本発明例）、曲線Ｂは試験Ｎｏ．１４（従来例）を示している。

【００３０】上記の実施例１より、セル壁の厚みが１５０μmの薄壁を有するコージェライト質セラミックハニカム構造触媒用担体において、１２００〜１３００℃の焼成温度領域で昇温速度を変化させてコージェライト質セラミックハニカム構造触媒用担体の細孔を微細化すること、すなわち、コージェライト質セラミックハニカム構造触媒用担体の固相反応が進む温度領域内である約１２００〜１３００℃の温度領域内で、昇温途中である１２５０〜１３００℃の昇温速度を、１２００〜１２５０℃の領域より５０℃／Ｈｒ以上遅くすることにより、気孔率が３５％以上と高く、さらにセル空間を含む担体容積あたりの質量が４００ｇ／リットル以下の従来にない軽量でありながら、Ａ軸圧縮強度を低下させることがないコージェライト質セラミックハニカム構造触媒用担体が得られることが明らかになった。

【００３１】（実施例２）表２の試験Ｎｏ．２（本発明例）、試験Ｎｏ．４（本発明例）、試験Ｎｏ．１４（従来例）、に示す昇温速度で焼成して得たコージェライト質セラミックハニカム構造触媒用担体を、実際にキャタリストとして組立て、このハニカム担体内に排ガスを流して速熱性について測定した。図２は、この測定結果であるキャタリストの入口と出口の排ガス温度と経過時間との関係を示すグラフである。図２において、キャタリストの出口の排ガスの出口温度の変化を示す曲線から明らかなように、約３０秒経過後に、従来例である試験Ｎｏ．１４と、本発明例である試験Ｎｏ．２、４とは、速熱性に差が生じ始め、触媒が活性化し始める温度である約２００〜２５０℃に到達する時間は、本発明の焼成方法で得たコージェライト質セラミックハニカム構造触媒

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用担体は、従来の焼成方法で得た担体と比較して、約８秒短縮されることが明らかになった。このように本発明例において速熱性が向上する理由は、直径０．５〜２μmの細孔が全細孔容積の３０％以上と微細な細孔の割合が高いこと、及びセル空間を含む担体容積あたりの質量が４００ｇ／リットル以下と軽量化されたために熱容量が低下したことによるものと推測される。

【００３２】以上に説明した上記本発明の実施の形態の説明において、セラミックハニカム構造触媒用担体のセル空間は四角セル形状について説明したが、本発明は四角セル形状の他、六角形、その他任意の形状にも適用できる。また、本発明のコージェライト質セラミックハニカム構造触媒用担体の断面形状は円形のみならず、楕円形状にも適用できる。

【００３３】

【発明の効果】本発明によれば、気孔率が３５％以上と高いために触媒担持性が良く、かつセル空間を含む担体容積あたりの質量が４００ｇ／リットルと軽量化されているために、熱容量が小さく速熱性が良好であり、しかも高いＡ軸圧縮強度を有しているために高い担体強度を有するコージェライト質セラミックハニカム構造触媒用担体を得ることができる。このため、コールドスタート時の触媒活性化までの時間を短縮でき、しかもキャニングによる圧力、及び熱衝撃による熱応力に対しても強く、極めて信頼性の高い、コージェライト質セラミックハニカム構造触媒用担体を提供することができる。

【図面の簡単な説明】

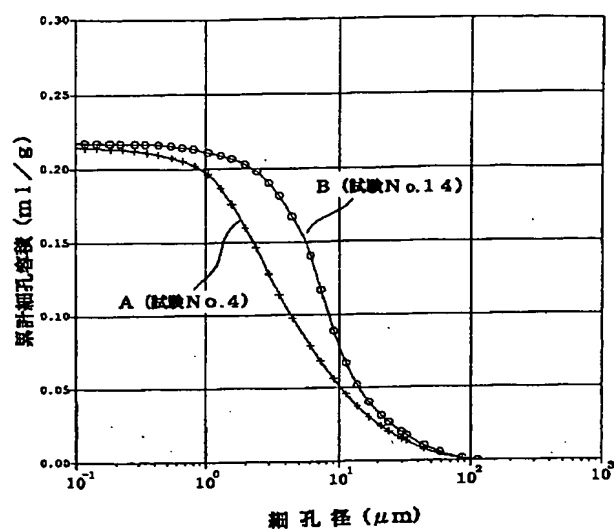【図１】　本発明の製造方法及び従来例の製造方法で製造したコージェライト質セラミックハニカム構造触媒担体の細孔直径と累計細孔容積との関係を示すグラフである。

【図２】　本発明及び従来例のコージェライト質セラミックハニカム構造触媒担体において、コールドスタート時の排気ガスの出口温度と経過時間との関係を示すグラフである。

【図３】　（ａ）はコージェライト質セラミックハニカム構造触媒担体の外観を示す図であり、（ｂ）は図３（ａ）のセル空間部の要部拡大図である。
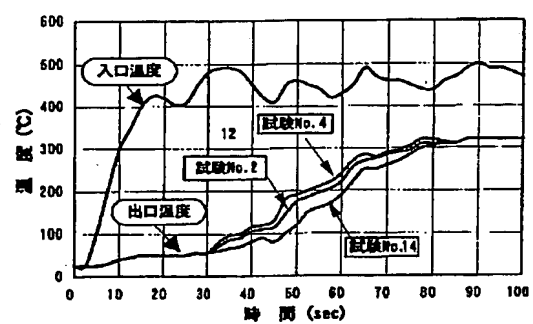
【符号の説明】

１：コージェライト質セラミックハニカム構造触媒用担体

２：セル空間

３：セル壁

４：周壁

【図1】

【図2】

【図3】

(a)

(b)